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THERMOPLASTIC COPOLYAMIDE AND COMPOSITION BASED THEREON

The present invention relates to a thermoplastic copolyamide and to a composition comprising this thermoplastic copolyamide as matrix, as well as to a process for manufacturing such a thermoplastic copolyamide.

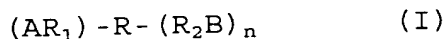
In the field of parts made of plastic, many parts are obtained by moulding a composition comprising a polyamide as matrix. The polyamides generally used are aliphatic, aromatic or semiaromatic linear polyamides.

The new processes for forming these compositions such as, for example, extrusion-blow moulding require compositions having a high melt viscosity so that the extruded part before blow moulding undergoes little or no deformation under the effect of its own weight. However, the mechanical, elastic and impact-strength properties of the parts must not be affected or only slightly so. Certain solutions have been proposed such as the use of high-viscosity linear polyamides obtained by post-condensation in the solid state, or by the addition of chain extenders. However, these solutions are often difficult to carry out or impair certain properties of the parts obtained.

The subject of the invention is a novel polyamide having a high melt viscosity, which may be obtained by a simple manufacturing process and with satisfactory mechanical properties, without the use of processes for increasing this viscosity which are either expensive and difficult to control or are detrimental to the properties of the manufactured part.

For this purpose, the invention proposes a novel copolyamide having a structure of the random-tree type.

This copolyamide is the result of the reaction between at least one monofunctional monomer satisfying the following general formula I:



in which:

-n is an integer greater than or equal to 2, preferably between 2 and 10 (limits inclusive),

-R₁, R₂ may be identical or different and represent a covalent bond or an aliphatic, arylaliphatic, aromatic or alkylaromatic hydrocarbon radical,

-R is a linear or branched aliphatic radical, a substituted or unsubstituted cycloaliphatic radical, a substituted or unsubstituted aromatic radical possibly comprising several aromatic rings and/or hetero atoms, or a

Sub B1

Sub B1

polymeric chain possibly containing
hetero atoms,

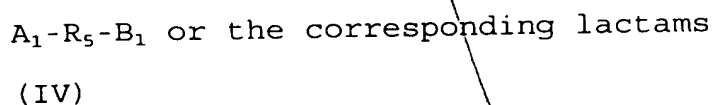
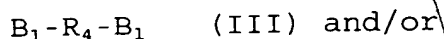
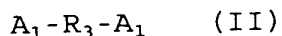
-A represents the amine or amine salt
functional group, or the acid, ester,
acid halide or amide functional group,

-B represents the amine or amine salt
functional group when A represents an
acid, ester, acid halide or amide
functional group, and an acid, ester,
acid halide or amide functional group
when A represents an amine or amine
salt functional group,

and at least one of the difunctional monomers of the
following formulae II to IV with, optionally, at least
one of the monofunctional monomers of the following
formulae V or VI, or with a prepolymer obtained from at
least one difunctional monomer of the following
formulae II to IV and, optionally, at least one
monofunctional monomer of the following formulae V or

VI,

-the difunctional monomers satisfying the
following general formulae:



-the monofunctional monomers satisfying the
following general formulae:

Sub B1 R_6-B_1 (V) and/or

R_7-A_1 (VI)

in which

5 $-A_1, B_1$ represent, respectively, an acid,
 ester or acid chloride functional group and
 an amine functional group or an amine salt,
 $-R_3, R_4, R_5, R_6, R_7$ represent substituted or
 unsubstituted, aromatic, linear or branched,
 alkyl hydrocarbon radicals or alkylaryl,
 10 arylalkyl, or cycloaliphatic radicals
 possibly including unsaturated groups.

According to a preferred characteristic of
 the invention, the radical R is an aromatic radical, $R_1,$
 15 R_2 each representing a covalent bond.

Moreover, the functional groups B and A in
 formula I are an acid functional group and an amine
 functional group, respectively, the acid functional
 group number n being advantageously 2.

20 Thus, suitable and preferred polyfunctional
 monomers of the invention are, especially, monomers
 thermally stable at a temperature greater than $150^\circ\text{C}.$
 By way of example, mention may be made of
 polyfunctional monomers in accordance with formula I in
 25 which R represents an aromatic radical such as
 aminophthalic acid, or a linear aliphatic radical such
 as the diacid 3-aminopimellic acid or the acid
 6-aminoundecanedioic acid. It is also possible to

mention α -amino acids such as aspartic acid and glutamic acid. Natural amino acids may also be used as polyfunctional monomer if their thermal stability is high enough.

5 Difunctional monomers of formulae II to IV are the monomers used for the manufacture of linear thermoplastic polyamides. Thus, mention may be made of ω -aminoalkanoic compounds comprising a hydrocarbon chain having from 4 to 12 carbon atoms, or lactams
10 derived from these amino acids, such as ϵ -caprolactam, saturated aliphatic dicarboxylic acids having from 6 to 12 carbon atoms such as, for example, adipic acid, azeleic acid, sebacic acid and dodecanoic acid, biprimary diamines, preferably linear or branched,
15 saturated aliphatic biprimary diamines having from 6 to 12 carbon atoms, such as, for example, hexamethylenediamine, trimethylhexamethylenediamine, tetramethylenediamine and m-xylenediamine.

Of course, mixtures of these monomers may be
20 used.

The preferred difunctional monomers of the invention are ϵ -caprolactam or hexamethylenediamine and adipic acid, or a mixture of these.

According to another characteristic of the
25 invention, the molar ratio of the monofunctional monomers of formula I to the sum of the difunctional monomers of formulae II to IV and monofunctional monomers of formulae V and VI is between 0.01 % and

5 The copolyamide of the invention has a melt flow index (MFI) of less than 5 g/10 minutes (measured at 275°C under a load of 2160 g) and, advantageously, a molecular-mass distribution index D of greater than 2.

The molecular-mass distribution index D is a
10 function of the degree of polymerization DP_n and of the
functionality factor F of the polymer.

The functionality factor F is calculated from the equation:

$$15 \quad F = 1 + \frac{N_2}{N_1 + N_2}$$

in which

$-N_2$ represents the number of moles of the polyfunctional compound,

20 -N₁ represents the number of moles of
 caprolactam or of difunctional monomer.

DPn is calculated from the following equation:

25 $DPn = \frac{A_2/B_2 - 1}{F - 1}$

in which

-B₂ represent the number concentration of NH₂ functional groups in the end polymer and
-A₂ represents the number concentration of COOH functional groups in the same end polymer.

5

The distribution coefficient D is given by the following formula:

$$D = \frac{A_2 / B_2 + 1}{F}$$

10

It is also possible to determine the number of branches of the hyperbranched polymer using the following formula:

$$R = B_2 / A_2 - 1 \text{ or } R = DP_n(F-1).$$

15

Thus, curves may be plotted which make it possible to determine the number of branches R and the distribution coefficient D as a function of the degree of polymerization DP_n for various values of the functionality factor F.

20

Examples of these curves are shown in the appended Figures 1a and 1b.

The copolymers of the invention also exhibit an improved impact strength as compared with linear polyamides obtained via the corresponding difunctional monomers. Thus, in the case of a copolymer obtained by using ε-caprolactam as the difunctional monomer, the

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impact strength of the copolyamide is greater than 60 J/m, while that of the corresponding linear polyamide, that is to say polycaprolactam, is less than 50 J/m.

5 Such copolyamides may be used in many applications such as the manufacture of moulded or injection-moulded parts.

 They are especially suitable for the manufacture of parts by extrusion-blow moulding
10 techniques. This is because the low melt flow index of the copolyamide makes it possible to limit the deformation of the parisons during their extrusion, before the blow moulding step.

 It is also possible to manufacture articles
15 from the copolyamides of the invention by injection-moulding processes. These articles exhibit markedly superior mechanical properties to those of articles obtained by injection moulding a composition based on a linear polyamide having the same melt flow index.

20 The copolyamide of the invention may also be used as the polymeric matrix for producing compositions comprising various additives or fillers for reinforcement or for filling.

 The subject of the invention is also a
25 composition, especially intended to be moulded in order to form parts or articles. This composition comprises, as polymeric matrix, at least one polyamide according to the invention and optionally other additives such as

moulding or demoulding aids, heat stabilizers, light stabilizers, antioxidants, fire retardants, pigments, colorants and lubricants.

The composition may also include agents which
5 improve the impact strength and/or filling or reinforcing fillers.

The compositions of the invention may also include, as polymeric matrix, in addition to the polyamide as described above, other thermoplastics such
10 as aliphatic linear polyamides or aromatic or semiaromatic polyamides, for example.

According to a characteristic of the invention, the compositions of the invention are obtained by mixing, generally in a single-screw or
15 twin-screw extruder, a polyamide according to the invention with the various additives, this mixing generally being carried out in the melt state of the polyamide, then by extruding the compound in the form of rods which are then cut into granules. Next, the
20 moulded parts are produced by melting the granules produced above and feeding the composition in the melt state into the appropriate moulding, injection-moulding or extrusion devices.

The subject of the invention is also a
25 process for manufacturing a copolyamide according to the invention.

In a first method of implementing this manufacturing process, a monomer mixture is produced

with predetermined proportions of each component. The said mixture is polymerized under conditions and according to an operating method which are equivalent to those used for the manufacture of the linear
5 polyamide corresponding to the difunctional monomers employed. Thus, when ϵ -caprolactam is employed, water is added to the monomer mixture in order to initiate the hydrolytic opening of the caprolactam.

According to a second method of implementing
10 the invention, a linear polyamide prepolymer is manufactured by the polycondensation of difunctional monomers in order to obtain a prepolymer having a number-average molecular weight \bar{M}_n of about 2000 to 3000, approximately.

15 The polyfunctional monomer is added to the linear prepolymer and the polymerization is continued either in the melt or in the solid state. This method of production makes it possible, in particular, to obtain hyperbranched copolyamides using polyfunctional
20 monomers that are thermally stable at relatively low temperatures, for example of less than 200°C, since the solid-state postcondensation is carried out at lower temperatures than those of the melt polymerization.

The polyfunctional monomer may be added into
25 an extruder or into a reactor, the solid-state postcondensation taking place under the conventional and usual conditions employed for that of linear polyamides.

According to another variant of this method of implementing the process for manufacturing a copolyamide according to the invention, the polyfunctional monomer is added with a catalyst, thus making it possible to carry out the reaction directly in the extruder. Suitable catalysts are the catalysts conventionally used for amidification reactions or reactions in which amide functional groups undergo polycondensation, such as, for example, phosphorus compounds.

Further details and advantages of the invention will be more clearly apparent in the light of the examples given below solely by way of illustration and in the light of the appended figures in which:

- Figures 1a and 1b show graphs comprising a number of curves for different values of the functionality factor F representing, respectively, the variation in the distribution coefficient D and in the number of branches R as a function of the degree of polymerization DP_n , and

- Figure 2 shows the variation in the melt flow index as a function of the relative viscosity of a linear polyamide and of a copolyamide according to the invention and corresponding to Examples B and 4.

Examples 1 to 3

The synthesis of a copolyamide according to the invention was carried out by adding predetermined

amounts of a polyfunctional monomer according to Formula I, namely 5-aminoisophthalic acid, into the reaction mass of ϵ -caprolactam of a conventional process for preparing nylon-6.

5 The polymerization reaction was carried out for 12 hours at 270°C in an inert atmosphere (nitrogen).

To initiate the polymerization, by hydrolytic scission of caprolactam, a small amount of water is
10 added to the reaction mixture.

For each polymer obtained, the relative viscosity η , the number concentration of amine and acid terminal groups, and the molecular-mass distribution factor D and the melt flow index (MFI) are measured.

15 This index is determined according to the ASTM D1238 standard under a load of 2160 g and at a temperature of 275°C.

The relative viscosity η is determined using a solution containing 1% by weight of polymer in 96%
20 sulphuric acid.

The distribution index D is a function of the degree of polymerization DP_n and of the functionality factor F of the polymer.

The numbers of amine and acid terminal groups
25 in the final copolyamide are determined by potentiometric analysis and are expressed in meq/kg of polymer.

Table I

Ex.	AIP molar %	H ₂ O wt. %	MFI g/10 min.	D	A meq/kg NH ₂	B meq/kg COOH	η
A	--	0.042	6.6	2	30.9	31.9	3.89
1	0.25	0.10	0.38	3	27	53.9	4.55
2	0.50	0.1	0.53	3.8	21	59.3	4.45
3	1.00	0.07	0.83	6.66	16.5	94	4.36

AIP: 5-aminoisophthalic acid

5 Examples 4 to 8

Tests carried out according to the operating method of Examples 1 to 3 with 0.5 mol.% of 5-aminoisophthalic acid were carried out with different polymerization times. The results are indicated in

10 Table II below.

Table II

Ex.	Polymerization time (h)	MFI g/10 min.	A ₂ (NH ₂) (meq/kg)	B ₂ (COOH) (meq/kg)	η
B	12	14.1	43.3	36.1	3.56
4	4	14.6	35.1	78.2	3.02
5	6	12.5	32.7	71.7	3.18
6	8	10.7	30.3	74	3.33
7	10	2.9	29.7	62.4	3.72
8	12	1.3	26.2	60.9	3.87

These results demonstrate that, in order to
 5 obtain a polyamide having a melt flow index equivalent
 to that of a linear polyamide, the polymerization time
 can be divided by 3. Moreover, the polyamide of the
 invention can have a melt flow index ten to twenty
 times lower than that of a linear polyamide. The
 10 variation in this melt flow index as a function of the
 viscosity is illustrated in the appended Figure 2.

The mechanical properties of the copolyamide
 obtained in Example 4 were determined on test pieces
 having a width of 12.57 mm, a thickness of 3.16 mm and
 15 a length of 50 or 80 mm. Table III below gives the
 results compared with a PA-6 linear polyamide.

Table III

Properties	Branched polyamide of Example 4	PA-6 linear polyamide
Relative viscosity	3.33	3.4
Number of NH ₂ terminal functional groups (meq/kg)	30	38
Number of COOH terminal functional groups (meq/kg)	74	37
IZOD impact strength (ASTM D256 standard) (J/m)	70.6	40-50
Flexural modulus (ASTM D638 standard) (N/mm ²)	2650	2750
Tensile strength (N/mm ²)	75.2	70
Elongation %	180	200